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STANFORD UNIV CALIF DEPT OF CHEMISTRY
METAL COMBUSTION PROCESSES AS STUDIED BY CHEMILUMINESCENCE AND --ETC(U)
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DAAG29-77-6-0151

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17 APR 15219.3-C

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A083641	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) METAL COMBUSTION PROCESSES AS STUDIED BY CHEMILUMINESCENCE AND CHEMI-IONIZA- TION		5. TYPE OF REPORT & PERIOD COVERED Final Report 7/1/77-2/1/80
7. AUTHOR(s) Richard N. Zare		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Stanford University Stanford, Ca. 94305		8. CONTRACT OR GRANT NUMBER(s) DAAG 29-77-S-0151
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) N/A		12. REPORT DATE 4/14/80
		13. NUMBER OF PAGES 6
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)
NA

18. SUPPLEMENTARY NOTES
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
80 4 23 077

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
The PbF A($\Omega=1/2$) - X $^2\Pi_1$ band system has been vibrationally reanalysed, based on the observation of 69 new bandheads. The singlet-triplet splitting in methylene (CH_2) has been estimated to be 8.1 ± 0.8 kcal/mole, based on the detection of $\text{CH}_2^+ \text{A}_1$ following the photolysis of ketene (CH_2CO). The band energies of BaI , SF_3 , and SF_4 have been determined to be 72.9 ± 2 , 91.1 ± 3.2 , and 84.1 ± 3.0 kcal/mole, based on the appearance of chemiluminescent reactions with metastable alkaline earth atoms. The two C_{10}H_8 isomers, azulene and naphthalene, have been distinguished in a mass spectrometer through the use of laser-controlled multiphoton ionization.

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METAL COMBUSTION PROCESSES AS STUDIED BY
CHEMILUMINESCENCE AND CHEMI-IONIZATION.

9 FINAL REPORT. 1 JUL 77-1 FEB 78

10 RICHARD N. ZARE

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U. S. ARMY RESEARCH OFFICE

15
CONTRACT NUMBER DAAG 29-77-G-0151

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FINAL REPORT

"Metal Combustion Processes as Studied by
Chemiluminescence and Chemi-ionization"

Contract Number:

DAAG 29-77-G-0151

Period:

July 1, 1977 - February 1, 1980

Name of Institution:

Leland Stanford Junior University

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Accession For	
NTIS - CHINA	<input checked="checked" type="checkbox"/>
NSC - TW	<input type="checkbox"/>
Departmental	<input type="checkbox"/>
Administrative	<input type="checkbox"/>
By _____	
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Summary of Research Highlights

The reaction $\text{Pb} + \text{F}_2$ has been studied under beam-gas conditions at F_2 pressures of 10^{-4} torr and in the presence of argon at ~ 7 torr. A series of 133 red degraded bandheads belonging to the $A(\Omega=\frac{1}{2})-X^2\Pi_{\frac{1}{2}}$ band system are observed; 69 of these bandheads are new and a vibrational reanalysis is made. The PbF A state is thought to be populated by the reaction of a metastable lead atom $\text{Pb}(^3\text{P}_1)$ or $\text{Pb}(^3\text{P}_2)$ with molecular fluorine.

By photodissociating ketene (CH_2CO) in the 3400-2900 Å region, singlet methylene (CH_2^1A_1) is detected by laser-induced fluorescence by observing the $\text{CH}_2^1\text{B}_1-^1\text{A}_1$ red band system. Under collision-free conditions a study of the appearance of $\text{CH}_2^1\text{A}_1(0,0,0)$ as a function of photodissociation wavelength and as a function of ketene temperature leads to a value for the heat of formation of singlet methylene:

$$\Delta H_{f0}^0(\text{CH}_2^1\text{A}_1) = 101.7 \pm 0.5 \text{ kcal/mole}$$

When this is combined with other known heats of formation, the singlet-triplet splitting is estimated to be 8.1 ± 0.8 kcal/mole, in good agreement with the most recent ab initio calculations of this quantity.

During this contract period we have constructed a pulsed source of metastable alkaline earth atoms, particularly $\text{Ba}(^3\text{D})$, $\text{Ca}(^3\text{P})$, and $\text{Sr}(^3\text{P})$. The metastable atoms traverse a scattering chamber filled with oxidant gas at low pressure (beam + gas arrangement) and the resulting chemiluminescence is analyzed

spectroscopically and as a function of the time elapsed between the formation of the metastables and the appearance of the chemiluminescence in the reaction/observation zone. This information is combined with known thermodynamic data to determine the bond energy of the gas molecule under study. In this manner we have found that

$$D_0^0(\text{BaI}) = 72.9 \pm 2 \text{ kcal/mole}$$

$$D_0^0(\text{F}_5\text{S-F}) = 91.1 \pm 3.2 \text{ kcal/mole}$$

$$D_0^0(\text{F}_3\text{S-F}) = 84.1 \pm 3.0 \text{ kcal/mole}$$

The latter two quantities may be combined with existing data to deduce the stepwise bond dissociation energies of SF_6 . A zigzag pattern appears in which the magnitude of the bond energy is larger for the even members. This behavior can be rationalized by a simple model which involves transformation of lone pair electrons on the central sulfur atom at first to a weak two-center three-electron bond and then to a strong three-center four-electron bond.

The possible use of laser ionization as an analytical detector has been explored by demonstrating the facile detection of the two C_{10}H_8 isomers, azulene and naphthalene. Compared to electron impact, multiphoton ionization provides more gentle ionization at low laser power and more extensive fragmentation at high laser power. Moreover, the efficiency of the latter exceeds that of the former during the time the laser is on. It would appear that this technique should make a useful addition to mass spectrometry.

Publications Supported Under DAAG 29-77-G-0151

C. R. Dickson and R. N. Zare, "Spectroscopic Study of $\text{Pb} + \text{F}_2$ Chemiluminescence," *Optica Pura by Aplicada* 10, 157 (1977).

R. K. Lengel and R. N. Zare, "An Experimental Determination of the Singlet-Triplet Splitting in Methylene," *J. Am. Chem. Soc.* 100, 7495 (1978).

R. C. Esther and R. N. Zare, "Determination of Bond Energies by Time-of-Flight Single-Collision Chemiluminescence," *Chem. Phys.* 28, 253 (1978).

T. Kiang, R. C. Esther, and R. N. Zare, "Upper and Lower Bounds on the $\text{F}_5\text{S-F}$ Bond Energy," *J. Chem. Phys.* 70, 12 (1979).

T. Kiang and R. N. Zare, "Stepwise Bond Dissociation Energies in Sulfur Hexafluoride," *J. Am. Chem. Soc.* (accepted for publication).

D. M. Lubman, R. Naaman, and R. N. Zare, "Multiplication Ionization of Azulene and Naphthalene," *J. Chem. Phys.* (accepted for publication).

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